

Preparation of 1,1,1,3,3-pentafluoropropane (HFC-245fa) by using a SbF₅-attached catalyst

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Abstract

In this report, a simple process for preparing HFC-245fa through the reaction of 1,1,1,3,3-pentachloropropane (PCP) and anhydrous HF via two-step vapor-phase catalytic fluorination is described. The antimony pentafluoride catalyst was supported on inert porous materials to improve the catalytic activity. The resulting process catalyst not only exhibited high catalytic activity and excellent thermo-stability, but also improved the performance of SbF₅, in terms of hygroscopicity and corrosion.

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Keywords: 1,1,1,3,3-Pentafluoropropane (HFC-245fa); Fluorinated catalyst; Vapor-phase catalytic fluorination; 1,1,1,3,3-Pentachloropropane; 1-Chloro-3,3,3-trifluoropropene

1. Introduction

1,1,1,3,3-Pentafluoropropane (HFC-245fa) is a non-ozone depleting compound with an acceptable global warming potential (GWP) [1]. Its 7.86-year lifetime indicates that it is not a long-lived atmospheric breakdown product [2]. Furthermore, this compound is not a volatile organic compound (VOC)[3,4], and it has low toxicity and is non-flammable, with a boiling point of 15.3 °C [5–7].

Therefore, HFC-245fa is considered as a third generation CFC replacement for HCFC-141b, a useful foaming reagent (used in insulation manufacturing) that is being phased out from use in developed countries since 2003 [8]. Production of HFC-245fa at an acceptable cost is the key to extending its practical application in industry. Currently, several synthetic routes of HFC-245fa are reported in the literature [9–13]. The main schemes are summarized in Fig. 1.

Among them, one of the simple routes to prepare HFC-245fa is by means of the catalytic fluorination of 1,1,1,3,3-pentachloropropane (PCP) with anhydrous hydrogen fluoride (AHF). In this method, the liquid-phase fluorination, in

which SbCl₅ is used as a catalyst, causes strong corrosion to the reactor and the resulting tar state products deactivate the catalyst [10,14]. The vapor-phase catalytic fluorination in which SbCl₅/C is used as the catalyst has excellent activity and selectivity [15]. However, since active charcoal is not stable at high temperature, the catalyst is easy to deactivate and difficult to regenerate. Therefore, most studies focused on investigating the catalyst in the vapor-phase catalytic fluorination process. Previously, we have reported some inert porous materials, such as porous aluminum fluoride (PAF), porous calcium fluoride (PCF), porous magnesium fluoride (PMF) and porous chromium fluoride (PCrF), and their application in preparing CFC alternatives based on their catalytic activity and inertness to gaseous fluorine and AHF [16–18].

Here with the help of these inert porous materials, we detail a facile procedure for preparing HFC-245fa by the reaction of PCP and AHF via a two-step vapor-phase catalytic fluorination in the presence of the inert porous materials. To improve the catalytic activity, antimony pentachloride was added to the porous materials. The catalyst fluorinated by HF not only exhibited high catalytic activity and excellent thermo-stability, but also improved the performance of SbF₅ regarding hygroscopicity and corrosion.

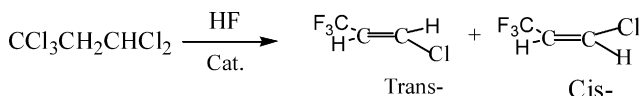
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2. Results and discussion

2.1. Preparation of CTFP from PCP

The preparation of HFC-245fa was carried out via vapor-phase catalytic fluorination in two steps. When the reaction of PCP with HF occurs in the presence of catalysts, *trans*-1-chloro-3,3,3-trifluoropropene (*trans*-CTFP) is formed predominately, as well as a small amount of *cis*-1-chloro-3,3,3-trifluoropropene (*cis*-CTFP) and a trace amount of 1,3,3,3-tetrafluoropropene (TFP). The scheme is below:



The reaction process is described as follows: first, the dechlorination of PCP occurred in the presence of Lewis acid to form $\text{CCl}_3\text{CH}=\text{CHCl}$. Then the CCl_3 in $\text{CCl}_3\text{CH}=\text{CHCl}$ was rapidly transferred into CF_3 to form $\text{CF}_3\text{CH}=\text{CHCl}$. Concurrently, a trace amount of $\text{CF}_3\text{CH}=\text{CHF}$ was produced. CTFP and TFP are the important intermediates in preparing HFC-245fa.

The results in Table 1 indicated that the yield of CTFP has no obvious change with the increase of amount of Sb wt% in the SbF_5/PAF from the reaction of PCP with AHF (see Table 1). It is attributed that the limited pore volume of PAF only absorbed a certain amount of SbCl_5 . Excess amount of SbCl_5 does not only take effect in the reaction, but also made the procedure for

Table 1

Fluorination of 1,1,1,3,3-pentachloropropane with the catalyst SbF_5 supported on PAF

Entry	SbCl_5 (wt%/PAF)	Reaction temperature (°C)	Yield (%)	
			<i>Trans</i> -CTFP	<i>Cis</i> -CTFP
1	12	315	51.0	6.3
		345	76.6	10.0
2	18	315	55.2	6.1
		335	75.9	8.3
3	25	305	51.1	3.7
		330	74.3	5.3

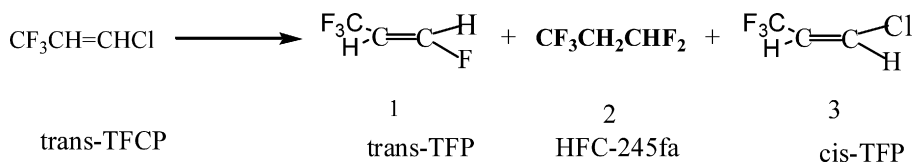
PAF: porous aluminum fluoride; CTFP, $\text{CF}_3\text{CH}=\text{CHCl}$. The yields of products were determined by ^{19}F NMR; SbCl_5 wt% supported on PAF.

different ratios (Table 2). The yield of CTFP increased with increasing Sb wt%. The catalytic activity of SbF_5/PCrF was higher than that of SbF_5/PAF (see Tables 1 and 2).

The results indicated that *trans*-CTFP is the predominate product in vapor-phase catalytic fluorination. This is in accordance with the E2 mechanism since the orientation of olefin-forming elimination depends on the steric requirements of transition states [19].

2.2. Preparation of HFC-245fa from CTFP

HFC-245fa was prepared as described in the procedure (Section 3.3.6). The scheme is as follows:



catalyst preparation difficult. The preferable wt% of SbCl_5 to PAF is less than 30%.

When the catalyst SbF_5/PCrF was applied to the reaction of PCP with AHF, *trans*-CTFP and *cis*-CTFP were obtained in

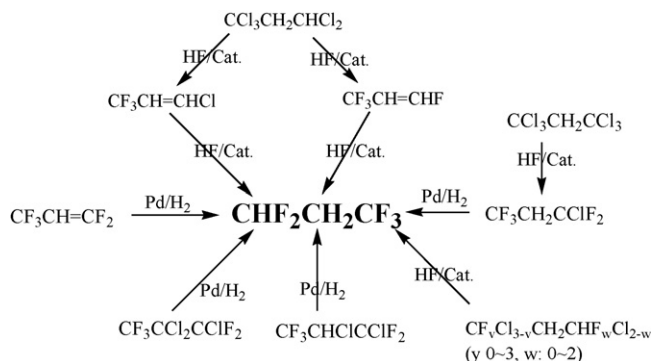


Fig. 1. Schemes for preparing 1,1,1,3,3-pentafluoropropane [9–13].

Table 2

Fluorination of 1,1,1,3,3-pentachloropropane with the catalyst SbF_5 supported on PCrF

Entry	SbCl_5 (wt%/PCrF)	Reaction temperature (°C)	Yield (%)	
			<i>Trans</i> -CTFP	<i>Cis</i> -CTFP
1	0	320	34.5	6.9
		340	56.1	5.6
2	20	305	50.0	7.1
		330	74.6	10.6
3	35	305	45.3	6.4
		330	80.0	11.3
4	50	305	89.8	9.0

PCrF: porous chromium fluoride; CTFP: $\text{CF}_3\text{CH}=\text{CHCl}$. The yields of products were determined by ^{19}F NMR; SbCl_5 wt% supported on PCrF.

Table 3
Preparation of HFC-245fa with the catalyst SbF₅ supported on PAF

Entry	Catalyst	Reaction temperature (°C)	Conversion (%)	Product selectivity GC area (%)		
				<i>Trans</i> -TFP	HFC-245fa	<i>Cis</i> -TFP
1	PAF	210	12.3	51.7	20.4	21.3
2	PAF	250	15.1	41.0	22.2	30.9
3	PAF	300	24.1	50.4	23.2	20.8
4	SbF ₅ /PAF	300	42.5	39.6	45.1	15.1
5	SbF ₅ /PAF	350	76.6	63.2	27.8	3.0

PAF: porous aluminum fluoride. The reaction mixture contained 300 ml CTFP and 30 ml HF; reaction contact time was 1.81 s.

Table 4
Preparation of HFC-245fa with the catalyst SbF₅ supported on PCrF

Entry	Catalyst	Reaction temperature (°C)	Conversion (%)	Product selectivity GC area (%)		
				<i>Trans</i> -TFP	HFC-245fa	<i>Cis</i> -TFP
1	PCrF	250	38.0	24.4	63.0	12.1
2	PCrF	280	62.0	33.1	60.2	6.5
3	PCrF	310	68.5	53.1	42.7	4.2
4	PCrF	340	66.9	57.9	36.5	5.5
5	PCrF	380	71.4	68.3	26.0	4.9
6	SbF ₅ /PCrF	250	48.4	26.0	65.0	8.6
7	SbF ₅ /PCrF	280	61.0	30.0	61.3	7.0
8	SbF ₅ /PCrF	310	69.0	40.8	54.5	4.5
9	SbF ₅ /PCrF	340	69.2	56.4	38.3	4.7

PCrF: porous chromium fluoride. The reaction mixture contained 300 ml CTFP and 30 ml HF; reaction contact time was 1.81 s.

Table 5
Preparation of HFC-245fa with the catalyst SbF₅ supported on PCF

Entry	Catalyst	Reaction temperature (°C)	Conversion (%)	Product selectivity GC area (%)		
				<i>Trans</i> -TFP	HFC-245fa	<i>Cis</i> -TFP
1	SbF ₅ /PCF	80	40.7	31.4	61.2	7.5
2	SbF ₅ /PCF	100	47.6	13.3	80.7	6.1
3	SbF ₅ /PCF	125	42.3	10.5	81.1	8.4
4	SbF ₅ /PCF	145	41.8	13.8	79.7	6.6

PCF: porous calcium fluoride. The reaction mixture contained 300 ml CTFP and 30 ml HF; reaction contact time was 1.81 s.

In the presence of Lewis acids such as the metal oxides and metal fluorides, the elimination of HF from HFC-245fa occurs easily at high temperature [20,21]. Therefore, the preparation of HFC-245fa via vapor-phase catalytic fluorination should be strictly controlled at a suitable reaction temperature to prevent the dehydrofluorination of formed HFC-245fa.

In our laboratory, various kinds of porous metal fluorides and SbF₅ supported on the above-mentioned metal fluorides were applied to the reaction (see Tables 3–6).

The results in Table 3 indicate that the antimony pentafluoride supported on PAF exhibited much more catalytic activity than PAF alone. The addition of antimony pentafluoride was advantageous to the conversion of CTFP and the formation

Table 6
Preparation of HFC-245fa with the catalyst SbF₅ supported on PMF

Entry	Catalyst	Reaction temperature (°C)	Conversion (%)	Product selectivity GC area (%)		
				<i>Trans</i> -TFP	HFC-245fa	<i>Cis</i> -TFP
1	SbF ₅ /PMF	80	46.1	19.2	74.8	6.0
2	SbF ₅ /PMF	100	58.7	11.8	83.8	4.4
3	SbF ₅ /PMF	120	63.2	10.1	86.5	3.4

PMF: porous magnesium fluoride. The reaction mixture contained 300 ml CTFP and 30 ml HF; reaction contact time was 1.81 s.

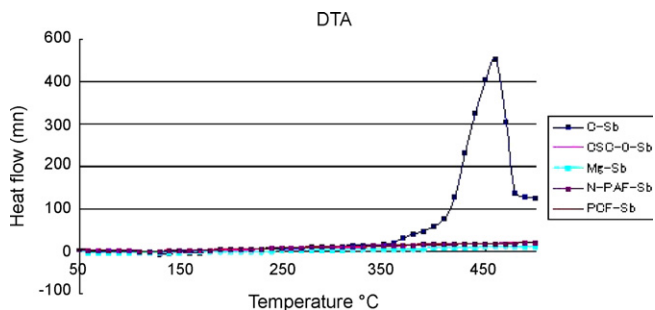


Fig. 2. DTA pattern of metal fluorides and active charcoal. Notes: SbF_5 /charcoal (C-Sb), SbF_5 /porous chromium cobalt fluoride (CSC-0-Sb), SbF_5 / MgF_2 (Mg-Sb), SbF_5 /porous aluminum fluoride (N-PAF-Sb), SbF_5 /porous calcium fluoride (PCF-Sb).

of HFC-245fa (entries 3 and 4 in Table 3). However, when the reaction temperature was about 300 °C, the selectivity of HFC-245fa decreased considerably although the conversion of CTFP increased from 42.5% to 76.6%.

The results in Table 4 show that the Cr-based catalyst required a higher reaction temperature for preparation of HFC-245fa. The addition of antimony to PCrF did not significantly affect catalytic activity in the reaction.

When porous calcium fluoride (PCF) and porous magnesium fluoride (PMF) were used as the catalyst support of antimony pentafluoride, the conversion of CTFP was about 50% and the selectivity for HFC-245fa was more than 80% at 100 °C (see Tables 5 and 6). The results were ascribed to the fact that PCF and PMF are relatively weaker Lewis acids than PAF and PCrF. The weaker Lewis solid acids, used as the support of the antimony-based catalyst, improved the selectivity of HFC-245fa.

2.3. Characterization of catalysts and their supports by DTA and TGA

The results of DTA indicate that the catalysts supported on porous metal fluoride keep an excellent thermo-stability until 500 °C; however, the catalysts supported on charcoal decompose at about 320 °C (Fig. 2). Although the initial activity of SbF_5 /charcoal was much higher than SbF_5 /porous metal

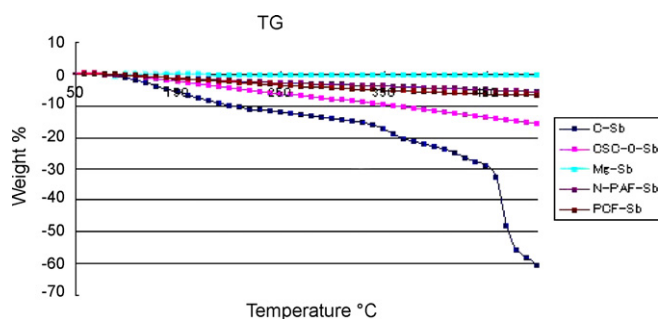


Fig. 3. TGA pattern of metal fluorides and active charcoal. Notes: SbF_5 /charcoal (C-Sb), SbF_5 /porous chromium cobalt fluoride (CSC-0-Sb), SbF_5 / MgF_2 (Mg-Sb), SbF_5 /porous aluminum fluoride (N-PAF-Sb), SbF_5 /porous calcium fluoride (PCF-Sb) [22].

fluoride, it was very difficult to regenerate because the catalyst deactivated in the reaction [15]; therefore, the SbF_5 supported on porous metal fluoride has an obvious advantage over SbF_5 supported on charcoal.

The investigation by means of TGA shows that SbF_5 catalysts supported on porous metal fluorides have much higher thermo-stabilities than those supported on charcoal.

The TGA results also indicated that antimony-based catalysts supported on metal fluorides are more stable than those supported on charcoal (Fig. 3). Among the metal fluoride catalysts, magnesium fluoride used as a catalyst support was the most stable. The order of stability of metal fluoride catalysts was as follows: porous magnesium fluoride > porous calcium fluoride > porous aluminum fluoride > porous chromium fluoride.

3. Experimental

3.1. Chemicals

1,1,1,3,3-Pentachloropropane was from Asahi Co., Japan. AHF was obtained from Kanto Denka Co., Japan. 1,1,1-Trifluoro-3-chloropropene (purity >99.0%) was purchased from SynQuest Lab. Inc., USA.

3.2. Instrument

The BET surface area and the distribution of pore diameter of samples were determined by means of low temperature adsorption of nitrogen using Micromeritics ASAP 2010. The sample was degassed under vacuum at 300 °C for 3 h before measurement.

^1H NMR and ^{19}F NMR of $\text{CCl}_3\text{CH}_2\text{CHCl}_2$, *trans*- $\text{CF}_3\text{CH}=\text{CHCl}$ and *cis*- $\text{CF}_3\text{CH}=\text{CHCl}$, *trans*- $\text{CF}_3\text{CH}=\text{CHF}$ and $\text{CF}_3\text{CH}_2\text{CHF}_2$ were recorded on a JNM-EX270 (JEOL, 270 MHz) at 25 °C with Me_4Si and CFCl_3 , respectively, as internal references in CDCl_3 solvent. The patterns were compared with those of authentic samples.

The GC-MS consisted of a Shimadzu GCMS-QP2010 and a Shimadzu GC-2010. The capillary column was Pora plot Q with 30 m length and 0.32 mm i.d. (film: 0.10 μm) from J & W Scientific Inc. The operating conditions of the GC were as follows: column temperature, 200 °C; detector temperature, 200 °C; carrier gas, $\sim 1\text{ cm}^3\text{ He/min}$; split ratio, 33:1; sample size, 5 μl ; pressure, 63 kPa.

DSC and TGA patterns were recorded on a Rigaku Thermoplus DSC-8230 and a Thermoplus 8120 equipped with an IBM PS/V Model 2411 (Master 100) computer.

The apparatus for the preparation of TFCP was composed of a pump for offering PCP, HF mass flow controllers and an electrically heated tubular Inconel reactor (14 mm in diameter and 300 mm in length) equipped with an inside Inconel tube for inserting type-K thermocouples with a 1-mm diameter. A thermocouple enters the reactor through a type-Monel CAJON[®] fitting and penetrates to the whole of the catalyst bed in order to measure the temperature change at different positions along the reactor.

The other set of apparatus for preparation of HFC-245fa consisted of two mass flow controllers (one for CTFP and the other for AHF) and the reactor used in the first step.

The product stream was scrubbed through a water bath at 60 °C to remove excess amounts of HF, passed through a drier filled with CaCl₂, and finally analyzed by a SHIMADZU GC-14 B on-line. The capillary column was Pora plot Q with 0.32 mm i.d. and 25 m length from J & W Scientific Inc. The operating conditions of gas chromatography (GC) were as follows—(a) preparation of CTFP from PCP: column temperature, 150 °C; detector temperature, 200 °C; injector temperature, 200 °C; carrier gas, ~5 cm³ He/min; sample size, 0.05 cm³. (b) Preparation of HFC-245fa from CTFP. The column was programmed as follows: initial temperature, 80 °C for 10 min; increasing the temperature at the rate of 20 °C/min to a final temperature of 200 °C for 10 min; detector temperature 200 °C; carrier gas, ~5 cm³ He/min; sample size 1.0 cm³.

3.3. Fluorination of 1,1,1,3,3-pentachloropropane and the preparation of process catalyst

3.3.1. Porous aluminum fluoride-based catalyst (PAF)

Porous aluminum fluoride-based catalyst (PAF), with 92 m²/g surface area, was prepared by reaction with AlF₃·3H₂O [16]. Then 25 g of SbCl₅ was dropped gradually into 25 g of the above PAF under a nitrogen atmosphere. The SbCl₅/PAF was charged into an Inconel reactor that was 300 mm in length and 12 mm in diameter, and dried at 100 °C for 3 h in the presence of nitrogen. Then AHF diluted by nitrogen was passed through the reactor at 200 °C (the diluted gas is a 1:1 mixture of N₂:AHF at 100 cm³/min) for 2 h, pure AHF 200 cm³/min for 3 h. Finally the remainder of AHF in the reactor was purged by nitrogen for 10 h.

3.3.2. Porous calcium fluoride-based catalyst (PCF)

Porous calcium fluoride-based catalyst (PCF), with 60 m²/g surface area, was prepared from the reaction of soda-lime and AHF [16]. Then 25 g of SbCl₅ was dropped gradually into 25 g of the above PCF under a nitrogen atmosphere. The SbCl₅/PCF was charged into a reactor as previously described (Section 3.3.1). The remainder of the procedure for preparing this catalyst was also as previously described (Section 3.3.1).

3.3.3. Porous magnesium fluoride-based catalyst (PMF)

Porous magnesium fluoride-based catalyst (PMF), with about 9.0 m²/g surface area, was prepared from commercial MgF₂. Then about 25 g of SbCl₅ was dropped gradually into 25 g of PMF under a nitrogen atmosphere. The SbCl₅/PMF was charged into a reactor as previously described (Section 3.3.1). The remainder of the procedure for preparing this catalyst was also as previously described (Section 3.3.1).

3.3.4. Porous chromium fluoride-based catalyst (PCrF)

Porous chromium fluoride-based catalyst (PCrF), with 90.0 m²/g surface area, was prepared from the reaction of porous chromia and AHF. Then about 25 g of SbCl₅ was dropped gradually into 25 g of PCrF under a nitrogen atmosphere. The SbCl₅/PCrF was charged into a reactor as previously described

(Section 3.3.1). The remainder of the procedure for preparing the catalyst was also as previously described (Section 3.3.1).

3.3.5. Preparation of CTFP from PCP

Preparation of CTFP from PCP was started by feeding PCP into the reactor via a vaporizer at 150 °C through a Masterflex (Cole-Parmer Instrument Co.) metering pump. AHF was drawn to vapor phase in the above vaporizer. The mixture of PCP and AHF passed through the reactor, which was packed with 10 cm³ of catalyst at the required temperature. The product stream from the reactor was scrubbed, dried and passed through the GC on-line. The results are listed in Tables 1 and 2.

3.3.6. Preparation of HFC-245fa from CTFP

Preparation of HFC-245fa from CTFP was as follows: A certain amount of AHF and CTFP were fed into a pre-mixture at 80 °C, then passed through a reactor packed with 10 cm³ of catalyst at the required temperature. The product stream from the reactor was scrubbed, dried and passed through the GC on-line. The results are listed in Tables 3–6.

3.4. Analytic results of intermediates and HFC-345fa

3.4.1. *Trans*-CF₃CH=CHCl

Boiling point, 51 °C/760 mmHg. Spectral data, MS peaks *m/e*: 61 ⁺CHCHCl; 69 ⁺CF₃; 82 ⁺CF₃CH; 95 ⁺CF₃CH=CH; 111 ⁺CF₂CH=CHCl, 130 ⁺CF₃CH=CHCl. NMR chemical shifts:

F1(3)δ-64.09 m; H2(1)δ-6.93 d,q; H3(1)δ-6.10 m.

3.4.2. *Cis*-CF₃CH=CHCl

Boiling point 21 °C/760 mmHg. Spectral data, MS peaks *m/e*: 61 ⁺CHCHCl; 69 ⁺CF₃; 82 ⁺CF₃CH; 95 ⁺CF₃CH=CH; 111 ⁺CF₂CH=CHCl, 130 ⁺CF₃CH=CHCl. NMR chemical shifts:

F1(3)δ-60.56 d; H2(1)δ-6.59 d; H3(1)δ-6.10 m.

3.4.3. *Trans*-CF₃CH=CHF

Boiling point –16 °C [23]. Spectra data, MS peak *m/e*: 45 ⁺CH=CHF, 69 ⁺CF₃, 95 ⁺CF₂CH=CHF, 114 ⁺CF₃CH=CH. NMR chemical shifts:

F1(3)δ-62.60 m, H2 (1)δ-5.67 m, H3(1)δ-7.19 d,d,q, F4(1)δ-120.4 d.

3.4.4. CF₃CH₂CHF₂

Spectra data of CF₃CH₂CHF₂: IR: 3001(w), 2359(w), 1307(vs), 1208(vs), 1146(vs). MS peak *m/e*: 51 ⁺CHF₂; 64 ⁺CHCHF₂; 69 ⁺CF₃; 115 ⁺CF₃CH₂CHF; 133 ⁺CF₃CH₂CHF. NMR chemical shifts:

F1(3)δ-63.86 m, H2(2)δ-2.72 m, H3(1)δ-6.07(t,t), F4(2)δ-116.38 (d,m).

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